

Review

Development of Ceria-Zirconia Solid Solutions and Future Trends

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Abstract

This review summarizes our achievements involved in developing oxygen storage materials in our laboratory, especially, our contributions to the enhancement of the oxygen storage capacity and the thermal stability improvement. In the 1980s, the first generation ceria-zirconia solid solution (CZ) was invented as a remarkable oxygen storage material for automotive catalysts. This material mainly consisted of about 20 mol% zirconia as the doping compound to ceria. To facilitate the valence change process from Ce^{4+} to Ce^{3+} causes to the enhancement of the oxygen storage capacity (OSC). In the 1990s, based on the benefit from the new technology which could dissolve more than 20 mol% zirconia in ceria, the second generation CZ were developed.

Subsequently, the third generation CZ (known as ACZ) was developed that further improved the thermal stability. Based on the concept of "Diffusion Barrier", ACZ was synthesized by adding alumina to CZ, in which the alumina acting as a diffusion barrier layer inhibited the coagulation of CZ and A at high temperature. By using oxygen storage materials, the automotive catalysts could efficiently reduce NO_x emission from automobiles. As a promoter of automotive catalysts, our progress with oxygen storage materials has made a great contribution to automotive catalyst development. Finally, a brief comment on the future trends related to oxygen storage materials is presented.

Keywords

Three-way catalyst, Oxygen storage material, Ceria-zirconia solid solution, Oxygen storage capacity, Alumina, NO_x emission

1. Introduction

Automotive three-way catalysts can simultaneously convert the three main pollutants in the exhaust gases, i.e., carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxides (NO_x) to CO₂, H₂O, and N₂, respectively. A three-way catalyst system was first put into practical use in 1977. Since then, the use of the three-way catalyst system has quickly spread. So far it has been implemented in production on almost all gasoline-powered vehicles.¹⁾ Our research has been centered on the technology of oxygen storage, broadly, from the screening to developing catalytic materials, including the precious metals, promoters and supports, etc. The objective of this technology are quickly to provide a massive amount of oxygen which will assist in the oxidation reaction and to eliminate any excess oxygen which will suppress the conversion of NO_x. Our idea is that the use of an oxygen storage material, will adsorb the oxygen coexisting with NO_x. This was regarded as an effective way to improve the NO_x conversion efficiency for a three-way catalyst, thus, we focused our research on the development of new oxygen storage materials, and targeted a significant enhancement in the oxygen storage capacity. Consequently, we made a pioneering breakthrough by development of the first generation ceria-zirconia solid solution (CZ).²⁻⁵⁾ By adding ZrO₂, the oxygen storage capacity (OSC) of CeO₂ and the thermal stability was significantly improved. Since it was announced, it has attracted a lot of attention around the world, and significant progress⁶⁻⁸⁾ has been made based on studies of its structure and physiochemical properties. In our laboratory, starting from CZ, the first generation, then the second generation of CZ⁹⁻¹²⁾ was developed, which recently proceeded to the third generation, ACZ. The progress and improvements in these materials is considered as the source for the enhancement of the three-way catalyst's performance.

In the present paper, we summarized our work involved in the development of the CZ oxygen storage material from the first generation to the third generation, and finally reviewed the recent and future research trends related to the CZ materials.

2. Fundamentals of three-way catalysts and the role of oxygen storage materials

The fundamental principles of the three-way catalysts are as follows: (1) The diluted pollutants are enriched on the surface of the catalyst; (2) With the assistance of the oxygen storage material, the exhaust atmosphere remains close to the stoichiometric ratio on the surface of the catalyst; and (3) The activity of the precious metal should be a maximum at the stoichiometric point. For fully exploiting the precious metal in the automotive catalysts, it is very important to maintain a proper atmosphere. No matter if oxygen is in excess or is limited in the exhaust, to reach 100% activity of the catalyst, it is very critical to ensure a stoichiometric ratio in the exhaust atmosphere. As a matter of fact, oxygen-rich and oxygen-depleted atmospheres occur during actual vehicle operation. To store oxygen in an oxygen-rich atmosphere and to release oxygen in an oxygen depleted atmosphere, a buffer between the lean-rich swings in the exhaust gas composition is highly expected, thus, an excellent oxygen storage material is very necessary for automotive catalysts.

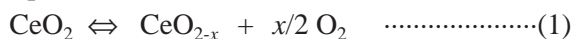
3. Development of a ceria-zirconia solid solution (CZ)

3.1 First generation CZ

We originally had an idea from the development of the oxygen sensor, especially from the phenomenon of oxygen migration in yttrium-stabilized zirconia (YSZ), a solid-state electrode for oxygen sensors. Initially, we worked on the oxygen storage function with zirconia containing bi-oxides. As the final result, we discovered that zirconia-ceria had an oxygen storage capacity. The mobility of the oxygen in YSZ is high in an electric field, but the valences of both the zirconium (+4) and the yttrium (+3) ions hardly change under any oxygen pressure. This implied that the level of oxygen defects is constant in pure oxides of ZrO₂ and Y₂O₃. We assume that the oxygen mobility in zirconia should be higher if stabilized by cerium ions. Moreover, due to the possible valence change of the cerium ion from 3+ to 4+ or from 4+ to 3+, it should have the ability to store more oxygen, thus, the up-down swings of the number of oxygen defects

accompanied with the valence change was achieved. Based on this idea, we set out to develop a new oxygen storage material.

Ceria stores oxygen under an oxygen-rich condition and releases oxygen under an oxygen-depleted condition. The valence of the cerium ion changes from 4+ to 3+ in an oxygen-depleted atmosphere (formula (1)).



The effective ionic radii of Ce^{4+} , Ce^{3+} and Zr^{4+} are 0.097, 0.114 and 0.084nm, respectively. During the oxygen storage and release process, the volume of the cerium compound increases in proportion to the change in the cerium oxidation state from Ce^{4+} to Ce^{3+} . The stress energy generated from this volume expansion would restrict any further valence change in the cerium. From this point, we expected that the introduction of the smaller size zirconium ions into the cerium framework would be able to compensate for the volume expansion, and facilitate the valence change process.

An accidental experimental error when we studied the relationship between the Ce/Zr ratio and the formed phases of oxides in CZ allowed us to discover that zirconia and ceria could form a solid solution if heat-treated up to 1000°C. **Table 1** summarizes the phase, lattice constant, crystallite size, and surface area data of the CZ with different zirconium contents. They were prepared by

impregnation of the CeO_2 powder in aqueous zirconia nitrate, followed by treatment at 1000°C. The lattice constant decreased with the zirconium content in the range $0 < x < 0.2$. This result indicated the formation of a cubic solid solution of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x < 0.2$). The data also suggested that the addition of zirconium prevented the grain growth of CeO_2 crystallites at high temperatures and improved the thermal stability of the CeO_2 . The first generation ceria-zirconia solid solution (CZ) was thus developed in 1987.

3.2 Second generation CZ

We then assumed that the oxygen storage capacity (OSC) of CZ would be enhanced with increasing amounts of zirconia dissolved in the ceria, thus, we tried to increase the amount of zirconia in the ceria, but the amount of zirconia dissolved in ceria could not exceed 20 mol% using a conventional method. At that time, another idea was generated, that is, the formation of the Zr-O-Ce combination in a solution containing cerium and zirconium, a very important precursor structure for our target compounds. Based on these two points, our research then proceeded ahead.

The lattice constants of CZ synthesized by using new method, which aimed at a homogeneous coprecipitation, are shown in **Fig. 1**. The constants were linear versus the zirconia content, which was in agreement with Vegard's law, and proved that the

Table 1 Phase formed in $\text{CeO}_2\text{-ZrO}_2$ ($\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$) system (1000°C).

x	Phase	Lattice Constant (nm)	Crystallite (nm)	Surface area (m^2/g)
0	CeO_2	0.5412	110	2.9
0.1	CeO_2 s.s.	0.5391	22	9.1
0.15	CeO_2 s.s.	0.5385	16	-
0.2	CeO_2 s.s.	0.5380	12	9.5
0.25	CeO_2 s.s.	0.5381	11	-
0.3	CeO_2 s.s.+ C1	0.5381	9	12.5
0.4	CeO_2 s.s.+ C1	-	-	-

s.s.: solid solution, C1: cubic fluorite-type oxide

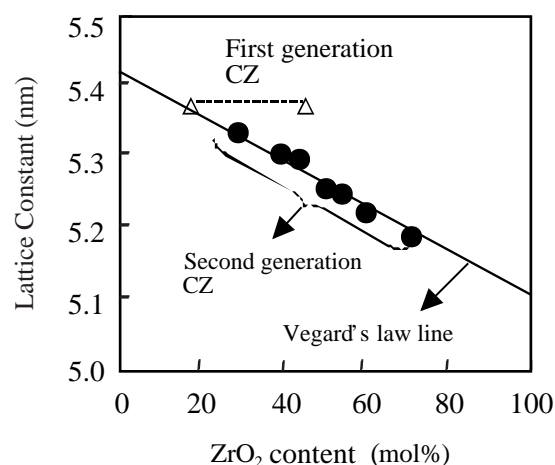


Fig. 1 Lattice constant of $\text{CeO}_2\text{-ZrO}_2$ solid solution as a function of ZrO_2 content.

material is a solid solution. Ceria and zirconia dissolved almost perfectly into each other in the second generation CZ, which was very different from the first generation CZ in terms of zirconia amount dissolved in the ceria. As a result, the OSC of the second generation CZ was about three times higher than that of the first generation CZ.

3.3 Third generation CZ

Figure 2 shows the new concept of a diffusion barrier. This was to improve the heat-resistance of the second generation CZ. The third generation CZ (ACZ), on this basis, was developed by inhibiting the coagulation or growth of the primary particles of the second generation CZ at high temperatures, by building alumina diffusion barrier layers between the primary particles, as shown in Fig. 2(a).

The particle diameter of the precious metal (Pt) and the crystal size of the CZ in the catalyst after an engine durability test were compared. The sintering of Pt on an ACZ-added catalyst was suppressed more effectively than that on the catalyst by using the second generation CZ. The crystal size with ACZ was also smaller than that with CZ. The specific surface area of the ACZ was greater than that of the second generation CZ after a durability test in air at temperatures of 900°C to 1200°C.

Figure 3 relatively indicated the progress of the storage and release activity per unit of cerium ion for

the first to third generation CZs, and compared to the pure ceria in the presence of Pt. As shown in the figure, the OSC value was much improved by increasing the solute amount and adding alumina. The catalysts containing the oxygen storage materials could significantly reduce the NO_x emission. Therefore, these oxygen storage materials have made a great contribution to catalytic systems for automotive exhaust gases.

4. The future trends

As mentioned above, the performance of oxygen storage materials was drastically improved through three generations of CZs, meanwhile, an improvement in the three-way catalysts by using CZ was achieved. For even cleaner exhaust emissions from automobiles, a better oxygen storage material is expected to be a prospective solution. Since the first appearance in 1989, a total of about 10 million new vehicles were equipped with the CZ containing the three-way catalysts. Important pointers for the enhancement of the OSC were proposed^{13, 14)} based on the X-ray absorption fine structure (XAFS) analysis of CZ at the atomic level. The model CZ compounds prepared by reduction at high temperature exhibited very high OSC efficiencies. It is noteworthy that almost all of the Ce in the model CZ contributed to the OSC. XAFS was also

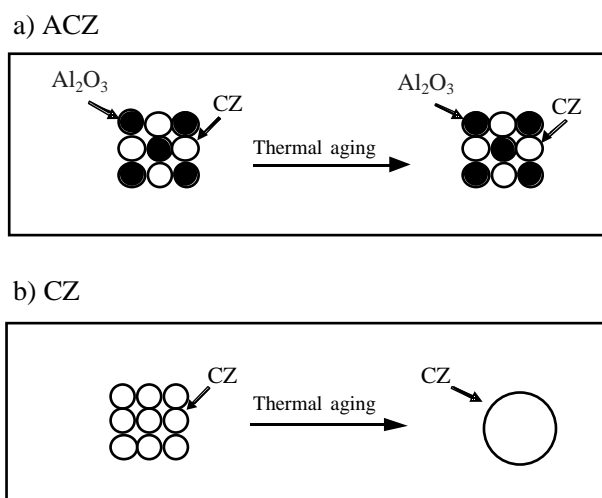


Fig. 2 Diffusion barrier concept.

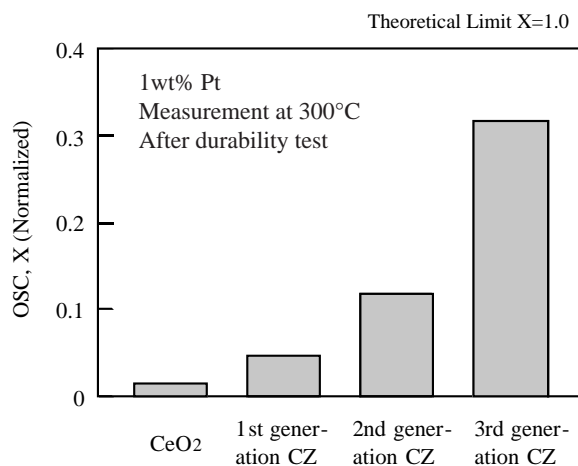


Fig. 3 Progress of OSC of a catalytic substrate after durability test.

employed to investigate the local structure around both the Ce and Zr in these CZ samples, to clarify the cation-cation network and the oxygen environment around the cations, thus to provide the information about the most ideal structure for the desired OSC. It was found that the OSC could be increased by improving the homogeneity of the Ce and Zr atoms in the CZ. It was postulated that an improvement in the homogeneity of the CZ and modification of the oxygen environment would be very critical for the OSC enhancement. **Figure 4** shows that the oxygen atoms to be stored or released were surrounded by zirconium atoms.

Our future efforts will concentrate on the improvement and development of a new generation, the fourth generation CZ, as our new goal. By developing new catalytic materials and new catalytic technology, we approach our goal of “zero-emission” of an automotive exhaust in the near future.

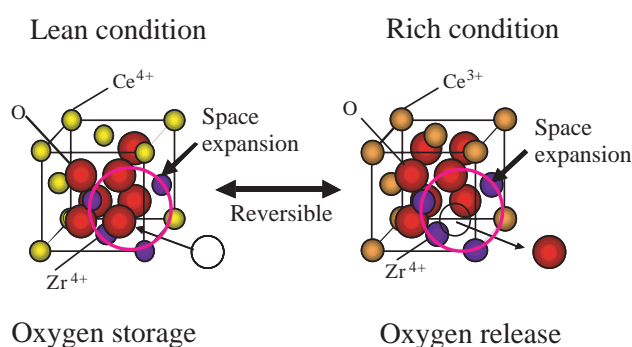


Fig. 4 Mechanism of oxygen storage and release.

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References

- 1) Matsumoto, S. : Toyota Tec. Rev., **44**-2(1995),10
 - 2) Matsumoto, S., et al. : JP No.2140560
 - 3) Matsumoto, S., et al. : Catal. Sci. Technol., (1991), 335, Kodansha
 - 4) Ozawa, M., et al. : R&D Rev. of Toyota CRDL, **27**-3 (1992), 43
 - 5) Ozawa, M., et al. : J. Alloys and Comp., **193**(1993), 73
 - 6) Kaspar, J., et al. : Catal. Today, **50**, (1999), 285
 - 7) Suda, A., et al. : J. Ceram. Soc. Jpn., **109**(2001), 177
 - 8) Tanabe, T., et al. : Stud. Surf. Sci. Catal., **138**(2001), 135
 - 9) Suda, A., et al. : JP No.3238316
 - 10) Sobukawa, H., et al. : Shokubai, **43**(2001),107
 - 11) Suzuki, T., et al. : The 88th Meet. of the Catal. Soc. of Jpn., (2001), 3A09
 - 12) Kanazawa, T., et al. : JSAE/SAE Int. Spring Fuel & Lubricants Meet., 20025084,(2002)
 - 13) Nagai, Y., et al. : Synchrotron Rad., **8**(2001), 616
 - 14) Nagai, Y., et al. : Catal. Today, **74**(2002), 225
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